

solute. $\gamma = a/N = f/f_0N$ where N is the mole fraction of the solute).¹¹

TABLE V

T, °C.	V. p. liq., atm.	Fugacity, liq., atm.	γ in CCl ₄	γ in CHCl ₃
HCl				
0	25.5	19.5	2.12	1.39
15	37.0	25.4		1.48
20	41.6	26.9	2.09	1.57
25	46.2	28.7	2.19	1.57
HBr				
0	12.3	11.1	1.44	1.19
15	18.1	16.2	1.36	1.12
25	23.0	20.2	1.29	1.10

The values for the fugacity of the pure liquid hydrogen chloride were estimated with the aid of vapor pressure and vapor density data,¹² and the approximate equation of Lewis and Randall for the fugacity.¹³ Since vapor densities of saturated hydrogen bromide vapor were not available, van der Waals equation with the constants calculated from critical constant data¹² was used for estimating the molal volumes of this gas for use in the Lewis and Randall equation. That the fugacity values obtained are at best only rough approximations is emphasized by the fact that when the experimentally determined density¹² of saturated hydrogen chloride vapor at 25° is used in the computation a value of 28.6 atm. is obtained in contrast to the value of 33.8 based on van der Waals equation. The calculation of O'Brien and

(11) Hildebrand, "Solubility," Reinhold Publishing Corp., New York, N. Y., 1936, p. 24.

(12) "International Critical Tables," Vol. III, p. 228.

(13) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Compounds," McGraw-Hill Book Co., New York, N. Y., 1923, p. 198.

co-workers gave 30.3¹⁴ atm. for this same quantity; and 18.3¹⁵ atm. for the fugacity of saturated hydrogen bromide vapor at 25° in contrast to the value of 20.2 calculated with the aid of van der Waals equation.

It is evident from the values of Table V that all of the solutions investigated show positive deviations from Raoult's law. In this respect carbon tetrachloride and chloroform then fall into a class with the mono-halobenzenes.¹⁶ References and discussion of attempts to correlate solubilities of compounds of the type dealt with in this paper with other physical properties of the solutions are given by the authors cited.¹⁶

Summary

1. The solubilities of hydrogen chloride and hydrogen bromide in carbon tetrachloride and in chloroform have been determined at 0, 15 and 25° at pressures below one atmosphere. The solubility in each case is proportional to the partial pressure of the solute. All of the solutions show positive deviations from Raoult's law.

2. The values for the solubility of hydrogen chloride in carbon tetrachloride given by Hamai are found to be too low and to show a false pressure dependence. A probable source of the error is suggested.

3. A solubility apparatus which offers certain advantages in the investigation of gaseous solutes which can be determined chemically is described.

(14) O'Brien, Kenny and Zuercher, *THIS JOURNAL*, **61**, 2504 (1939).

(15) O'Brien and Bobalek, *ibid.*, **62**, 3227 (1940).

(16) O'Brien and Byrne, *ibid.*, **62**, 2063 (1940).

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Conductance of Hydrochloric Acid in Aqueous Solutions from 5 to 65°

BY BENTON BROOKS OWEN AND FREDERICK HUMPHREY SWEETON¹

The purpose of this study was to investigate the conductance of hydrochloric acid in water as a function of temperature over a very wide concentration range. The data in dilute solutions are useful in the study of weak electrolytes and the extrapolated limiting conductances supplement the series of values obtained by Owen and Waters²

(1) This communication embodies part of the thesis presented by Frederick Humphrey Sweeton to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy (1941).

(2) B. B. Owen and G. W. Waters, *THIS JOURNAL*, **60**, 2371 (1938).

in dioxane-water mixtures at various temperatures. In the more concentrated solutions the data show a remarkable decrease in the effect of concentration upon both the conductance and its variation with temperature. At the highest concentrations the proton exchange mechanism, which explains the high mobility of the hydrogen ion, would be seriously affected by proton-chloride ion combination and possibly hindered by combination of the chloride ion with water. The meas-

urements were made at 10° intervals from 5 to 65° , and extend from about 0.001 to nearly $12 N$.

Apparatus and Technique

Cell 24, illustrated in Fig. 1, was constructed of Jena 16^{III} glass and was employed in the study of dilute solutions. At a given temperature measurements were made after successive additions of stock solution to a weighed amount of solvent in a 3-l. "solution flask" (not shown) equipped with ground glass connections. Mixing was accomplished, without loss of vapors at the higher temperatures, by forcing the same sample of air back and forth through the cell by means of the mercury column. The volumes of the bulbs and of the mercury were adjusted to prevent solution from passing beyond the safety bulb above the cell and air from rising into the solution flask. Flexible glass spirals permitted agitation and swirling of the solution flasks.

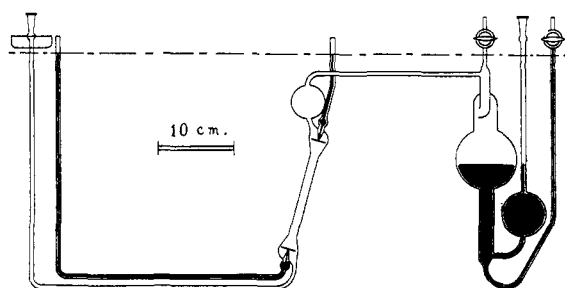


Fig. 1.—Diagram of Cell 24, showing disposition of leads and mercury column used to force air into cell.

Since it was important to have the air passage between the cell and the mercury column continuous and completely submerged in the oil-bath and to dispose the lead tubes so as to avoid Parker effects,³ the cell system was so fragile that it had to be permanently attached to a wooden frame to prevent breakage. The cell was cleaned in place by rinsing with distilled water until complete removal of hydrochloric acid was established by conductance. The system was dried before use by passing clean dry air through it.

The electrodes were 25 mm. in diameter and lightly platinized according to the procedure of Jones and Bollinger.⁴ A small Parker effect was present (about 0.003% for 70,000 Ω at 1000 cycles), but it was always determined by measuring the resistance at several frequencies³ and the results were corrected accordingly.

Cells 20 and 21, illustrated in Fig. 2, were constructed of Pyrex glass except for the uranium glass bulbs immediately surrounding the electrodes. These cells were used in the investigation of the concentrated solutions, which involved measurements at each given molality over the whole temperature range. The electrodes were platinum disks 25 mm. in diameter, lightly platinized.⁴ The variation in apparent conductance caused by changing the frequency from 4000 to 500 cycles was never greater than 0.05% and usually less than 0.02%. Correction was made for this effect.³

Solutions intended for use in Cells 20 and 21 were pre-

pared by delivering the proper quantity of one of the stock solutions (A or B) into a weighed amount of water in the 250-cc. solution flask illustrated in Fig. 2. In the preparation of the more concentrated solutions (from stock solution A), delivery was made through the loose central tube, and just beneath the surface of the water. The water surface outside of the central tube was covered with 10 cc. of mineral oil. Distribution experiments showed that this oil could not absorb enough acid to cause a concentration error greater than 0.01%. The oil and central tube were dispensed with in the preparation of moderately concentrated solutions from stock solution B.

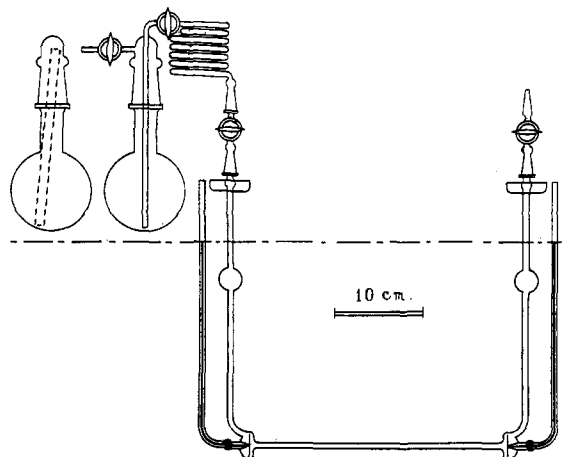


Fig. 2.—Diagram of Cells 20 and 21, showing disposition of leads and solution flasks.

The cell solution was thoroughly mixed, the flask connected to the cell and the solution forced through the cell by air pressure. After successive rinsings were shown to produce a change in conductance of less than 0.01% at 5° , the stopcocks were closed and readings taken at 10° intervals up to 65° . Check readings at fifteen minute intervals showed that equilibrium was established at each temperature. Air bubbles, which sometimes formed in the capillary cell chamber at high temperatures, could be removed by causing a small amount of solution to flow through the cell.

After completing the measurements at 65° the temperature was lowered to 5° to check the reproducibility of the run. The largest discrepancy found was 0.02%, except in the case of the most concentrated solution (15.8879 M) where the difference was 0.16%. This exceptional error was probably produced by escape of acid at the higher temperatures in spite of our precautions, but, in the absence of conclusive proof of this, the accuracy of the results for this concentration should not be considered better than 0.16% at any temperature.

The constant of Cell 24 was determined at 25° with 0.1 demal potassium chloride according to the procedure of Jones and Bradshaw.⁵ It was redetermined at several intervals and with two independently prepared samples of potassium chloride. No appreciable differences were found in duplicate determinations. The constants at other temperatures were calculated from the coefficient of

(3) G. Jones and G. M. Bollinger, *THIS JOURNAL*, **53**, 411 (1931).

(4) G. Jones and D. M. Bollinger, *ibid.*, **57**, 280 (1935).

(5) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

linear expansion of Jena 16^{III} glass given by Morey.⁶ The values are given by the equation

$$\text{Cell Constant } (K_{24}) = 28.138 (1 - 0.80 \times 10^{-5}t) \quad (1)$$

The constant of Cell 20 was determined with 1 demal⁶ potassium chloride at 25°. The values at this and other temperatures are given by the equation

$$\text{Cell Constant } (K_{20}) = 1207.4 (1 - 0.37 \times 10^{-5}t) \quad (2)$$

based upon the linear coefficient of Pyrex glass given by Morey.⁷

The constant of Cell 21 was determined by comparison with Cell 24, both filled with the same 0.069542 *M* solution of hydrochloric acid (see Table III). The equation

$$\text{Cell Constant } (K_{21}) = 1203.3 (1 - 0.37 \times 10^{-5}t) \quad (3)$$

represents the results of this comparison at six different temperatures (5 to 55°) within 0.02%. A direct determination of K_{21} against a 1 demal potassium chloride solution checked this equation at 25°. An exact cross check between Cells 20 and 21 was not made, but it is apparent from Table III that at $c^{1/2} \approx 1.4$ and $c^{1/2} \approx 2.02$ the concentrations covered by the two cells are so nearly the same that no serious inconsistency between K_{20} and K_{21} could remain unobserved.

The electrical measuring equipment consisted of a Dike⁸ bridge built after the design of Jones and Josephs⁹ and operated by a vacuum tube oscillator operating at 500, 1000, 2000, and 4000 cycles. The null point was detected by head phones through a tunable amplifier. All readings made with Cells 21 and 24 were corrected for bridge calibration, and for polarization¹⁰ and Parker⁹ effects, but those made with Cell 20 were uncorrected for these errors.

The temperatures were measured with a platinum resistance thermometer. The actual measurements were not made at the recorded even temperatures, but at several temperatures within three or four hundredths of a degree from these values.¹¹ All results recorded in this paper, cell constants as well as conductivities, have been corrected to even temperatures which we believe to be accurate to $\pm 0.01^\circ$.

Materials and Stock Solutions.—The conductivity water used in all measurements on dilute solutions (Table II) and in the determination of cell constants had a specific conductivity between 0.2×10^{-6} and 0.5×10^{-6} mho at 25°. The laboratory distilled water used in all other measurements, and in the preparation and analysis of stock solutions, had a specific conductivity of about 1.2×10^{-6} mho. No chloride ion was detectable.

Two commercial c. p. "analyzed" samples of potassium chloride were recrystallized three times from conductivity water, dried over calcium chloride and then heated suc-

cessively three days at 80 to 90°, and two days at 150 to 200°. They were then fused (and cooled) in platinum utensils, one in an electric muffle furnace and the other over a gas burner. The gas heated sample gave a faint alkaline reaction with phenolphthalein, but cell constants determined with the two samples were practically identical.

Stock solution A was a 5-liter sample of J. T. Baker "C. P., analyzed" hydrochloric acid. According to the manufacturer's analysis, the sum of the impurities classed as non-volatile matter (iron, heavy metals, free chlorine, sulfur trioxide, arsenic and sulfate ion) was less than 0.002%. No attempt was made to purify this acid further. It was originally intended for use in the study of very concentrated solutions only, but preliminary measurements in dilute solutions at 25° gave results in such close agreement with those obtained with freshly redistilled acid in this Laboratory and elsewhere,¹² that it was used as the source of acid for all other stock solutions. Gravimetric analysis, as silver chloride, gave the composition of solution A as 36.68% HCl by weight. The solution was stored in an all-glass system which included two saturators in series, so that all air drawn into the storage flask contained the proper amount of hydrochloric acid and water vapor. Stock solution A was diluted directly in the preparation of all cell solutions of concentrations greater than 4 *M*, with the single exception of the 4.4545 *M* solution.

Stock solution B was made by dilution of solution A, but was independently analyzed for chloride at the beginning and end of the measurements. The first analysis gave 24.403, 24.415 and 24.412%, and the second gave 24.408, 24.413 and 24.410% HCl by weight. The value 24.410 was used for all calculations. This solution was stored in an all-glass system, but did not require saturators or elaborate precautions to prevent change in composition during transfer to weight burets, because the composition of the vapor was practically identical with that of the liquid at room temperatures.

The several stock solutions used in the measurements on dilute solutions (Table II) were prepared by dilution of Solution B without independent analysis.

Vacuum corrections were made for all weighings, and the weights were carefully compared with a recently certified standard. Corrections also were made for the solubility of silver chloride in the course of the analyses. It is believed that the concentrations of solutions prepared from solution A are in error by less than $\pm 0.05\%$, and those prepared from solution B are in error by less than $\pm 0.025\%$.

Calculations and Results

In the calculation of normalities from molalities, use was made of the equations

$$c = \frac{1000m}{\varphi m + 1000 v_0} \quad (4)$$

and

$$\varphi = \varphi^0 + k \sqrt{m} \quad (5)$$

The last equation was used by Åkerlöf and Teare¹³ to express their values of the apparent molal volumes of hydrochloric acid solutions over a

(6) G. W. Morey, "Properties of Glass," Reinhold Pub. Corp., New York, N. Y., 1938, p 286.

(7) G. W. Morey, *loc. cit.*, p. 289.

(8) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

(9) G. Jones and R. C. Josephs, *THIS JOURNAL*, **50**, 1049 (1928).

(10) The polarization varies with the square root of the reciprocal of the frequency [G. Jones and S. M. Christian, *ibid.*, **57**, 272 (1935)] and the Parker effect varies with the square of the frequency. These two effects were separated graphically by successive approximations. Since their sum rarely exceeded 0.03 or 0.04%, an exact analysis of these errors was not attempted.

(11) This was due to an uncertainty in the calibration of the temperature resistance bridge which was not eliminated until after the conductance measurements were completed.

(12) T. Shedlovsky, *THIS JOURNAL*, **54**, 1411 (1932).

(13) G. Åkerlöf and J. W. Teare, *ibid.*, **60**, 1226 (1938).

wide concentration range. Interpolated values of φ^0 and k at the appropriate temperatures are recorded in Table I along with values of v_0 , the specific volume of water.¹⁴

TABLE I

$t, ^\circ\text{C}.$	PARAMETERS USED IN THE CALCULATIONS				
	φ^0	k	v_0	α^*	β^*
5	16.807	0.8970	1.00001	0.2205	34.87
15	17.484	.8237	1.00087	.2237	46.53
25	17.980	.7837	1.00294	.2277	59.86
35	18.296	.7771	1.00598	.2322	74.81
45	18.432	.8038	1.00985	.2374	90.99
55	18.388	.8638	1.01448	.2431	107.93
65	18.163	.9571	1.01979	.2493	126.38

The parameters α^* and β^* of the Onsager¹⁵ equa-

$$\Lambda = \Lambda^0 - (\alpha^* \Lambda^0 + \beta^*) \sqrt{c} \quad (6)$$

tion are also given in Table I. The fundamental constants and viscosity values used in the evaluation of these parameters were taken from the International Critical Tables,¹⁴ but the dielectric constants were those reported by Wyman.¹⁶

The experimental results obtained at low concentrations with Cell 24 are recorded in Table II. The values under the heading $\Lambda^{0'}$ were calculated by the equation

$$\Lambda^{0'} = \frac{\Lambda + \beta^* \sqrt{c}}{1 - \alpha^* \sqrt{c}} \quad (7)$$

and used in the evaluation of Λ^0 by the method of Shedlovsky.¹⁷ The extrapolation at 25° is illustrated in Fig. 3. Shedlovsky's¹² results have been adjusted to the standard of Jones and Bradshaw⁵

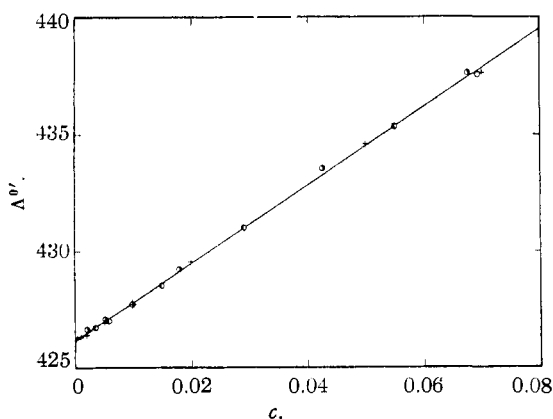


Fig. 3.—Determination of Λ^0 at 25° by the extrapolation of Shedlovsky: ● and ○, the authors' results from Table II; ○, the authors' result at the lowest concentration in Table III; +, Shedlovsky's results.

(14) "International Critical Tables." McGraw-Hill Book Co., New York, N. Y., 1931.

(15) L. Onsager, *Physik. Z.*, **27**, 388 (1926); *ibid.*, **28**, 277 (1927).

(16) J. Wyman, Jr., *Phys. Rev.*, [2] **35**, 623 (1930).

(17) T. Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1932).

and included in the figure for comparison. Our results are in very good agreement with those of Shedlovsky over the whole concentration range, and have been arbitrarily extrapolated to the value $\Lambda^0 = 426.16$ obtained by Shedlovsky. Although this value might truly represent the "best" linear extrapolation of all the data shown in Fig. 3, it has little physical justification unless the absolute error in the concentration of the stock solution is less than $\pm 0.01\%$ and the temperature is known to better than $\pm 0.005^\circ$. Incidentally, the rounded value, 426.2, is more probable in a physical sense than the lower value, 426.16, for two reasons. In the first place, it has been shown¹⁸ that the Shedlovsky extrapolation leads to low values of Λ^0 because of the neglect of a term in $c \log c$. The error from this cause is very small for 1-1 electrolytes, but a tendency for the lower end of the experimental curve to bend upward is indicated in Fig. 3. In the second place Saxton and Langer¹⁹ independently obtained the value 426.27, on the Jones and Bradshaw⁵ standard. Values of Λ^0 at other temperatures will be found in Table IV. Values of Λ have been carried out to five figures, because there is some justification for believing that the relative accuracy of c is a little better than 0.01% in a given series of measurements.

The experimental results obtained with concentrated solutions are recorded in Table III. The two series of measurements on the most dilute solution, made with Cells 21 and 24, indicate that the constants of these cells, as given by equations (3) and (1), are satisfactorily consistent at all temperatures concerned. The difference between any corresponding pair of values is the magnitude of the errors which might arise from temperature fluctuations and the uncertainties in the corrections for polarization, etc. These differences show no definite trend with temperature. Consideration of the difference (0.10) between the two values of Λ for the most dilute solution at 55°, and the experimental difficulties encountered with the most concentrated solutions, leads us to assign an uncertainty of 0.1 conductance unit to all values in Table III. The figure in the next decimal place has been recorded as an aid to graphical interpolation and the estimation of temperature coefficients. A few interpolated values of Λ obtained from large scale plots are given in Table

(18) B. B. Owen, *ibid.*, **61**, 1393 (1939).

(19) B. Saxton and T. W. Langer, *ibid.*, **55**, 3638 (1933).

TABLE II
OBSERVED CONDUCTANCES OF HYDROCHLORIC ACID AT LOW CONCENTRATIONS^a

$c \times 10^3$	$c^{1/2}$	Λ	Λ^0	5°	$c \times 10^3$	$c^{1/2}$	Λ	Λ^0
1.0582	0.03253	294.66	297.94		0.7757	0.02785	294.89	297.69
1.8444	.04055	293.80	297.88		1.9719	.04441	293.28	297.74
2.7875	.05280	292.70	298.01		4.2711	.06535	291.49	298.06
5.6198	.07497	290.71	298.26		8.8018	.09382	289.10	298.55
12.468	.11166	287.80	299.06		16.786	.12956	286.48	299.55
					38.926	.19730	282.03	302.05
					83.418	.28881	277.10	306.70
				15°				
1.0552	0.03248	358.27	362.42		9.4605	0.09726	350.83	363.26
2.2824	.04777	356.28	362.38		26.186	.16182	344.85	365.61
4.5919	.06776	353.96	362.60		52.528	.22918	339.57	369.16
9.0866	.09532	351.03	363.21		81.873	.28613	335.36	372.52
19.085	.13815	346.93	364.62					
40.646	.20160	341.80	367.77					
73.192	.27054	336.95	372.05					
				25°				
2.0725	0.04552	419.50	426.65		3.4430	0.05868	417.49	426.70
5.0678	.07169	415.83	427.09		5.8852	.07676	414.91	426.97
9.8731	.09936	412.14	427.76		14.873	.12195	409.33	428.53
17.868	.13367	408.15	429.22		28.868	.16991	404.14	430.99
42.590	.20637	400.80	433.52		54.926	.23436	398.08	435.34
67.518	.25984	396.16	437.61		86.364	.29388	393.14	440.19
				35°				
1.1158	0.03340	483.03	489.32		0.9498	0.03082	483.57	489.38
3.2193	.05674	479.09	489.78		2.2900	.04785	480.63	489.65
6.4180	.08011	475.25	490.36		5.2170	.07223	476.73	490.36
16.981	.13031	467.95	492.60		9.7983	.09899	472.61	491.31
30.653	.17508	462.31	495.55		20.607	.14355	466.49	493.68
45.016	.21217	458.16	498.60		36.641	.19141	460.64	497.05
62.122	.24924	454.43	502.14		54.971	.23446	455.94	500.74
				45°				
3.4473	0.05872	538.33	551.36		2.0697	0.04550	540.59	550.68
9.3811	.09685	531.23	552.74		4.7045	.06859	536.16	551.38
24.164	.15545	521.94	556.62		9.9479	.09974	530.53	552.69
50.811	.22541	512.51	563.15		21.525	.14672	523.07	555.78
90.257	.30043	503.75	571.87		39.319	.19828	515.86	560.27
					54.591	.23365	511.39	563.93
				55°				
3.8052	0.06169	594.76	610.58		1.8318	0.04280	599.03	609.99
7.7232	.08788	589.21	611.77		4.4463	.06668	593.72	610.82
24.419	.15627	576.47	616.77		9.9570	.09978	586.86	612.49
47.108	.21728	566.81	623.18		24.102	.15557	576.62	616.74
70.116	.26498	560.24	629.38		45.354	.21297	567.53	622.76
					63.454	.25190	562.18	627.82
				65°				
2.6807	0.05178	652.59	667.75		0.9830	0.03135	658.17	667.35
5.4171	.07360	646.93	668.50		2.4799	.04980	653.27	667.86
13.781	.11739	636.98	671.46		4.7662	.06904	648.34	668.57
30.006	.17322	625.93	677.06		12.825	.11324	638.03	671.29
50.526	.22478	616.95	683.67		24.883	.15774	629.02	675.52
71.522	.26743	610.27	690.08		55.372	.23531	615.61	685.56

^a Measured with Cell 24.

TABLE III
OBSERVED CONDUCTANCES OF HYDROCHLORIC ACID AT HIGH CONCENTRATIONS

Cell	m	m ^{1/2}	5°		15°		25°	
			c ^{1/2}	Λ	c ^{1/2}	Λ	c ^{1/2}	Λ
21	0.069542	0.26371	0.26355	278.05	0.26343	337.08	0.26316	395.55
24	.069542	.26371	.26355	277.99	.26343	337.10	.26316	395.55
21	.069614	.26384	.26372	278.04	.26360	337.15	.26332	395.60
21	.124113	.35230	.35196	273.49	.35180	331.39	.35142	388.59
21	.440343	.66358	.66113	257.61	.66076	311.51	.66001	364.82
21	.812105	.90117	.89490	242.86	.89430	293.32	.89323	343.44
21	1.08920	1.04365	1.03392	232.66	1.03306	280.91	1.03177	328.83
21	1.4646	1.2102	1.1948	219.64	1.1938	264.93	1.1922	310.12
21	2.0284	1.4264	1.3988	201.54	1.3974	242.78	1.3954	284.20
20	2.0958	1.4477	1.4212	199.38	1.4197	240.15	1.4177	281.14
20	2.6695	1.6339	1.5956	182.87	1.5938	219.97	1.5914	257.46
20	3.2355	1.7988	1.7476	168.06	1.7455	201.88	1.7427	236.22
20	4.4322	2.1053	2.0231	141.32	2.0202	169.24	2.0165	197.85
21	4.4545	2.1106	2.0278	140.82	2.0248	168.61	2.0212	197.09
20	6.8926	2.6254	2.4675	100.64	2.4629	119.85	2.4578	139.78
20	8.3423	2.8883	2.6796	83.43	2.6742	99.14	2.6682	115.52
20	10.4334	3.2301	2.9418	64.95	2.9352	77.06	2.9280	89.75
20	12.3335	3.5119	3.1460	52.81	3.1384	62.64	3.1303	72.98
20	15.8879	3.9860	3.4643	38.06	3.4552	45.17	3.4456	52.70

Cell	35°		45°		55°		65°	
	c ^{1/2}	Λ	c ^{1/2}	Λ	c ^{1/2}	Λ	c ^{1/2}	Λ
21	0.26275	452.56	0.26225	507.60	0.26165	560.30
24	.26275	452.57	.26225	507.55	.26165	560.40
21	.26292	452.60	.26242	507.66	.26182	560.31
21	.35089	444.33	.35021	498.11	.34941	549.06	0.34851	598.31
21	.65898	416.71	.65770	466.69	.65621	514.30	.65454	559.47
21	.89178	392.29	.89004	439.43	.88803	484.41	.88581	527.10
21	1.03007	375.71	1.02805	421.03	1.02574	464.37	1.02318	505.52
21	1.1902	354.47	1.1878	397.51	1.1852	438.72	1.1820	478.16
21	1.3930	325.07	1.3902	364.90	1.3871	403.24	1.3837	439.89
20	1.4152	321.60	1.4124	361.07	1.4092	399.09	1.4058	435.32
20	1.5885	294.70	1.5852	331.21	1.5814	366.49	1.5779	400.07
20	1.7394	270.51	1.7357	304.30	1.7319	337.15	1.7278	369.11
20	2.0125	226.67	2.0084	255.35	2.0036	283.49	1.9990	311.06
21	2.0171	225.81	2.0128	254.36	2.0082	282.42	2.0035	309.81
20	2.4523	160.17	2.4467	180.77	2.4409	201.32	2.4352	221.72
20	2.6620	132.38	2.6555	149.53	2.6492	166.78	2.6429	184.05
20	2.9208	102.88	2.9134	116.38	2.9061	130.07	2.8989	143.93
20	3.1221	83.74	3.1139	94.85	3.1057	106.22	3.0978	117.84
20	3.4358	60.63	3.4260	69.00				

IV along with the limiting conductances referred to in the preceding paragraphs.

of inflection at about 0.25 and 3.5 N. Both of these points appear to shift to lower concentra-

TABLE IV

EQUIVALENT CONDUCTANCE OF HYDROCHLORIC ACID AT EVEN VALUES OF \sqrt{c}

\sqrt{c}	5°	15°	25°	35°	45°	55°	65°
0	297.6	362.0	426.2	489.2	550.3	609.5	666.8
0.5	266.2	322.1	377.4	431.1	482.8	531.9	578.2
1.0	235.2	284.0	332.3	379.4	424.9	468.2	509.2
1.5	192.0	230.9	270.0	308.6	346.1	382.1	416.3
2.0	143.5	171.6	200.1	228.6	256.9	284.2	310.8
2.5	97.9	116.0	134.7	153.6	172.5	191.2	209.5
3.0	61.3	72.2	83.5	94.9	106.6	118.2	130.0

The general behavior of conductance as a function of concentration and temperature is illustrated in Fig. 4. The curves pass through points

TABLE V

TEMPERATURE COEFFICIENT OF THE EQUIVALENT CONDUCTANCE, $\frac{100}{\Lambda} \left(\frac{\partial \Lambda}{\partial T} \right)_c$

At 5 and 65° the values at infinite dilution are about 2.18 and 0.85, respectively.

\sqrt{c}	15°	25°	35°	45°	55°
0	1.78	1.49	1.27	1.10	0.96
0.5	1.73	1.44	1.22	1.04	.91
1.0	1.71	1.42	1.22	1.05	.90
1.5	1.69	1.43	1.24	1.06	.92
2.0	1.65	1.42	1.24	1.08	.95
2.5	1.59	1.40	1.23	1.09	.97
3.0	1.54	1.36	1.22	1.10	1.01

tions as the temperature is lowered. The absolute change in conductance with either concentration or temperature is least in the most concentrated solutions. Table V shows that the influence of concentration upon the relative change in conductance with temperature is very slight at 35 and 45°, but becomes more pronounced at lower temperatures. The temperature coefficients given in this table were determined graphically from plots of sensitive deviation functions.

Ionic Mobilities.—Harned and Dreby²⁰ have recently determined the transference number of the hydrogen ion in hydrochloric acid solutions at 5° intervals from 0 to 50°. Their data, combined with the conductances recorded in the preceding sections, have been used to calculate the limiting ionic mobilities given in Table VI. The

TABLE VI
LIMITING IONIC MOBILITIES AND THEIR TEMPERATURE COEFFICIENTS

	λ^0		$\frac{100}{\lambda^0} \left(\frac{\partial \lambda^0}{\partial T} \right)_c$	
	H ⁺	Cl ⁻	H ⁺	Cl ⁻
5	250.6	47.0	2.02	2.99
15	300.9	61.2	1.65	2.39
25	349.9	76.3	1.37	2.05
35	396.7	92.5	1.15	1.80
45	440.8	109.5	0.97	1.60
55	482.1 ^a	127.4 ^a	.83 ^a	1.44 ^a
65	520.8 ^a	146.0 ^a	.72 ^a	1.31 ^a

^a Extrapolated transference numbers were used in the estimation of this value.

results at 55 and 65° required an extrapolation of the transference data beyond 50°, but, since the variation of the latter with temperature is practically linear, the error in extrapolation is presumably small.

A comparison of the mobilities of the hydrogen and chloride ions shows that the absolute temperature coefficient, $(\partial \lambda^0 / \partial T)_c$, of the chloride ion *increases* from 1.405 at 5° to 1.753 at 45°. This increase is about 20% of the value of the coefficient at 45°. Under the same conditions, $(\partial \lambda^0 / \partial T)_c$ for the hydrogen ion *decreases* about 18%. Although the dissimilarity in the behavior of these ions could be accounted for by the maximum estimated²⁰ error in the transference numbers, it should not be overlooked on this account.

(20) H. S. Harned and E. C. Dreby, *THIS JOURNAL*, **61**, 3113 (1939).

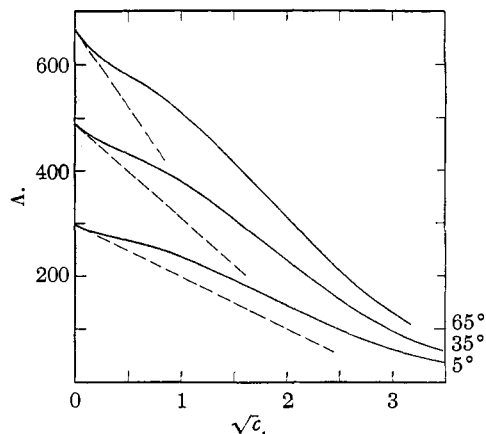


Fig. 4.—Equivalent conductance of hydrochloric acid as a function of concentration: upper curve, 65°, middle curve 35°, lower curve, 5°. Broken lines represent the limiting law, equation (6).

The method by which Harned and Dreby smoothed their results gave a value of T^0_+ in excellent agreement with that of Longworth²¹ at 25°, and there is little reason to suspect that the value obtained at 45°, by the consistent use of this method, is not equally precise. The effect of the estimated error in Λ upon the temperature coefficient of the mobilities is negligible compared to that of the transference numbers.

Summary

The conductance of hydrochloric acid in water was determined and tabulated at 10° intervals from 5 to 65°, and at concentrations between 0.001 and 15 *M*. The limiting conductance, Λ^0 , was evaluated at each temperature.

Values of Λ and their temperature coefficients are tabulated at even values of \sqrt{c} , and at several temperatures.

By combining these results with transference numbers from the literature, a table of ionic mobilities, and their temperature coefficients, is constructed. It is noted that the temperature coefficient of the chloride ion mobility appears to increase with temperature, contrary to the behavior of the hydrogen (and other) ions. The contribution of experimental errors to this anomaly is discussed.

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(21) L. G. Longworth, *ibid.*, **54**, 2741 (1932).